

A Review of Modification Method of Cathode Materials for High-performance Lithium-ion Batteries

— Ternary lithium-rich materials

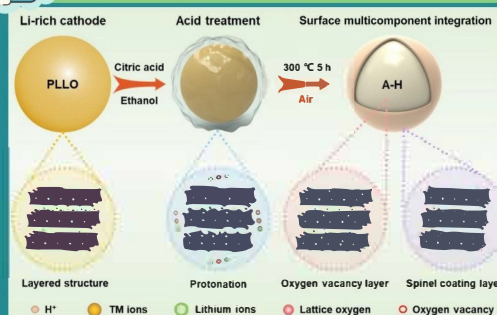
Abstract

Lithium-rich cathode materials have garnered significant attention due to their ultra-high theoretical energy density and reversible capacity, making them promising candidates for next-generation lithium-ion batteries powering electric vehicles and portable electronics. These materials offer advantages such as high operating voltage and good specific capacity. However, practical challenges including capacity and voltage attenuation, lattice oxygen release, irreversible structural changes, and low ionic conductivity hinder their widespread commercialization. Modification methods can improve the redox reversibility, structural stability, and overall cycling performance of the cathode material.

Introduction

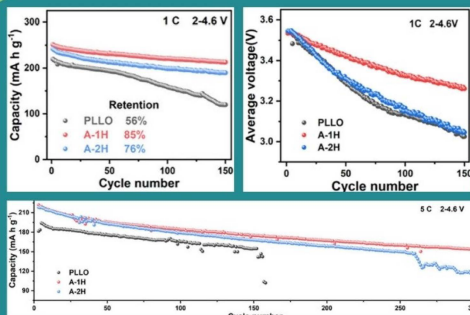
Lithium-rich cathode materials, known for their high energy density and capacity, suffer from practical challenges including capacity and voltage decay, lattice oxygen release, irreversible structural changes, and poor rate performance. These issues significantly limit their commercialization. To address these challenges, researchers have developed various strategies such as oxygen vacancy introduction, ion doping, surface coatings, and comprehensive modifications to enhance their structural stability, redox reversibility, and ionic conductivity. This study explores these techniques with the aim of improving the electrochemical performance of lithium-rich cathode materials.

Method1. Introduction of oxygen vacancies

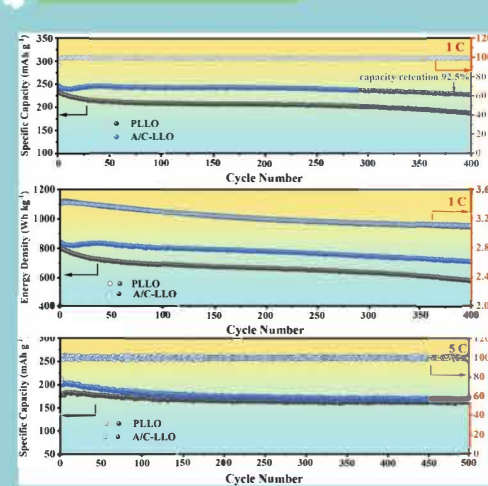


Scheme 1. Citric acid reacts with the material to produce oxygen vacancies [1]

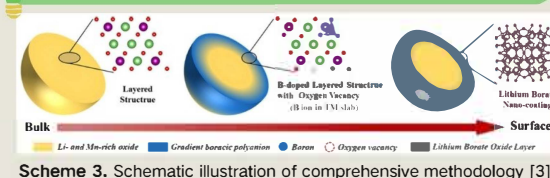
The citric acid treatment of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ dissolves lithium and oxygen on the surface, creating oxygen vacancies. This lowers the oxygen partial pressure, reducing the formation of molecular oxygen and reactive oxygen species, with concentrations linked to treatment duration. During calcination, these vacancies cause the rearrangement of manganese and lithium ions, partially converting the Li_2MnO_3 phase into a spinel phase with 3D lithium-ion diffusion channels. This enhances lithium-ion diffusion and surface stability. Together, these mechanisms improve redox processes and reduce irreversible oxygen release.



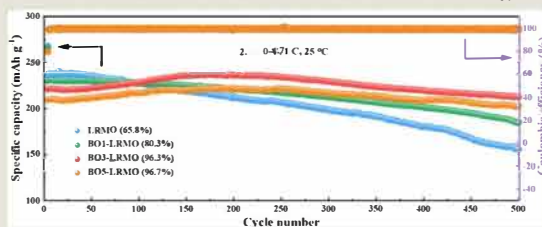
Method2. Fe³⁺ doping



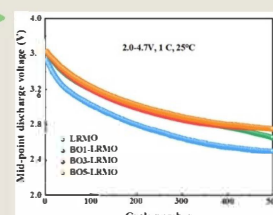
Method3. Oxygen vacancies, B-doping, boronic acid coating



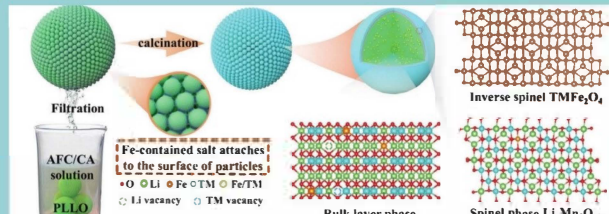
Scheme 3. Schematic illustration of comprehensive methodology [3]



A three-in-one modification strategy was applied to the $\text{Li}_{1.2}\text{Mn}_{0.53}\text{Ni}_{0.20}\text{Co}_{0.07}\text{O}_2$ cathode using H_3BO_3 treatment. Upon high-temperature decomposition, H_3BO_3 produces B_2O_3 and oxygen atoms that enter the LRMO lattice, forming B-O bonds and creating oxygen



vacancies. Gradient B doping lowers non-hybridized O 2p states' energy, enhances hybrid redox reversibility, and stabilizes peroxide species, preventing irreversible oxygen release. Additionally, B_2O_3 reacts with surface Li to form a $\text{Li}_2\text{B}_4\text{O}_7$ coating, which isolates the electrode from the electrolyte, reducing side reactions and preventing transition metal dissolution, thereby maintaining structural and electrochemical stability.



Scheme 2. The redox chemistry of surface lattice oxygen is synergistically regulated by Fe doping and the spinel protective layer [2]

Fe^{3+} doping forms strong Fe-O bonds, stabilizing lattice oxygen. Electrons from the oxygen 2p orbitals partially transfer to the Fe 3d orbitals, lowering the activation energy for oxygen and enhancing the reversibility of oxygen redox reactions, thus preventing oxygen release. During deep delithiation, Fe^{3+} not only replaces some lithium but also redistributes transition metal ions, suppressing lattice phase transitions and improving stability. Additionally, Fe doping creates a spinel phase on the surface, further stabilizing lattice oxygen and reducing harmful interfacial side reactions.

Method4. Mn₃O₄ coating



Scheme 4. The synthesis process diagram of Mn₃O₄ surface modified LRMO material [4]

The Mn_3O_4 coating on $\text{Li}_{1.2}\text{Ni}_{0.27}\text{Mn}_{0.54}\text{O}_2$ increases oxygen vacancies, suppressing oxygen release and reducing irreversible capacity loss in initial cycles. It also enhances Li^+ diffusion and rate capability. During cycling, Mn_3O_4 converts to LiMnO_2 through redox reactions, with Mn^{2+} release causing Mn and O atoms to rearrange. This rearrangement mitigates Jahn-Teller distortion, stabilizing the lattice and preventing structural collapse.

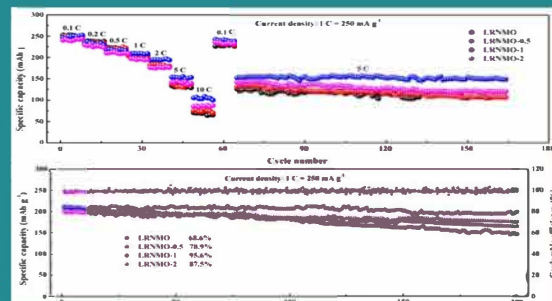


Table 1 Effect of different surface strategies on electrochemical performance of Li-rich cathode materials.

Li-rich cathodes	Modification strategy	Capacity after Cycles (1C) [mAh/g]	Capacity Retention (1C) [%]	Voltage Decay per Cycle (1C) [mV]	Discharge Capacity (5C) [mAh/g]	Capacity Retention (5C) [%]
Li-rich cathode	Citric Acid Treatment	213.5(150 cycles)	85	1.62	154.1(300 cycles)	69.4
Li-rich cathode	Fe ³⁺ doping	228(400 cycles)	92.5	0.78	168(500 cycles)	95.3
Co-free Li-rich Mn-based cathode	Mn ₃ O ₄ coating	200.8(200 cycles)	95.6	150.0	150.0(initial)	—
Li-rich cathode	Three-in-one modification strategy	212.9(500 cycles)	96.3	1.73	>160(initial)	—

Conclusion

The study evaluated various modification strategies for cathode materials, finding that Fe^{3+} doping showed excellent performance. It achieved a discharge capacity of 228 mAh g⁻¹ after 400 cycles at 1 C with a retention rate of 92.5%, and maintained a capacity of 168 mAh g⁻¹ even after 500 cycles at 5 C. The voltage retention rate was 90.8%, with low voltage decay of 0.78 mV per cycle. This approach opens up new possibilities for developing high-performance Li-rich cathodes.

[1] Y. Fang et al., "Boosting rate performance of layered Lithium-rich cathode materials by oxygen vacancy induced surface multicomponent integration," *Journal of Energy Chemistry*, Jan. 2024, doi: 10.1016/j.jechem.2023.12.050.

[2] H. Wu et al., "Lattice oxygen redox reversibility modulation in enhancing the cycling stability of Li-Rich cathode materials," *Advanced Functional Materials*, vol. 33, no. 41, Jun. 2023, doi: 10.1002/adfm.202303707.

[3] C. Wu et al., "Enhancing performances of Co-free Li-rich Mn-based layered cathode materials via interface modification of multiple-functional Mn₃O₄ shell," *Chemical Engineering Journal*, vol. 431, p. 134208, Mar. 2022, doi: 10.1016/j.cej.2021.134208.

[4] J. Guo et al., "Triggering Cationic/anionic Hybrid Redox Stabilizes High-temperature Li-rich Cathodes Materials via Three-in-one Strategy," *Energy Storage Materials*, vol. 69, p. 103383, May 2024, doi: 10.1016/j.ensm.2024.103383.